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THE RÔLE OF SURFACE TENSION AND CONTACT ANGLE IN THE PERFORMANCE OF SPRAY LIQUIDS[1,2]

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INTRODUCTION

The wetting and spreading properties of spray liquids have been defined by Martin (*16*)[4] as follows:

(*a*) *Wetting properties* are defined by the ability of the liquid to form a persistent liquid-solid interface when excess of liquid is drained from the surface and are assessed by the receding contact angle. Perfect wetting results when this angle is zero. ($\cos \Theta_r = 1$.)

(*b*) *Spreading properties* are defined by the ability of the liquid to form a persistent liquid-solid interface solely by surface activity over the plain solid surface, and are *a function of the advancing contact angle.*

Both wetting and spreading are functions of the contact angle, in one case the receding[5] angle, and in the other case the advancing angle.

In the course of experimental work on the insecticidal efficiency of various aqueous solutions the writer has become interested in the spreading and penetrating properties of the liquids as indicated by their advancing contact angle.

An attempt has been made to devise a means of contact-angle measurement which would combine practicability with the great accuracy

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[4] Italic numbers in parentheses refer to "Literature Cited" at the end of this paper.

[5] When a drop of liquid is placed on a solid, it may either spread over the surface of the solid in a thin film or it may come to rest before spreading out into a film, in which case there is a contact angle between the surface of the liquid and the solid. This angle is called the *advancing* contact angle. If sufficient liquid is withdrawn from the drop flattening it further, or if the drop is inclined the *receding* contact angle is formed.

necessary for measurements of the low contact angles common to all spray oils as well as to aqueous solutions with low surface tension. The present paper includes an explanation of this method and a presentation of results of experiments relating to differences in the contact angles of various liquids; the influence of various types of substrata and the effect of the addition of solutes are also considered.

The writer is aware of the fact that the static contact angle may not be an accurate criterion of the wetting and spreading ability of a liquid under the dynamic conditions existing when a spray is being applied. Ben-Amotz and Hoskins (*2*), by comparing the static and dynamic behavior of oil emulsions on beeswax surfaces, have shown that although oil emulsions containing 0.0225 per cent sodium oleate have a much lower static contact angle than those with equivalent concentrations of blood albumin and hemoglobin, they do not wet as well when applied as a spray.

Nevertheless, after a spray liquid is applied to a surface, its further spread and its penetration into masses of waxy threads, such as cover mealybugs and aphid colonies, or its penetration into the spiracles of insects, under the bodies of scale insects, and into plant tissues is influenced by its advancing contact angle under more or less static conditions. This follows from the laws of capillary flow, and can be proved experimentally, as will be shown later. Consequently, in connection with many of the entomological problems involving the use of sprays, contact angle is a good index of the physical qualifications of the spray liquid.

PREVIOUS METHODS OF CONTACT-ANGLE MEASUREMENT

Stellwaag (*20*) utilized a principle, worked out by H. P. Wilson (see Sulman, *21*), in determination of the contact angles of various spray liquids on leaf surfaces and insect integuments. The liquid to be tested was placed in a container, and the solid (leaf surface, insect integument, etc.) was attached to a device for holding it and dipping it into the liquid until the surface of the liquid was exactly horizontal at the point of contact with the solid. The image of the object was reflected on a mirror upon which was etched a protractor; from this the contact angle could be read. This method was adopted, with refinements, by English (*9*).

O'Kane *et al.* (*17*) devised a method of photographing a drop of spray liquid in contact with the integument of an insect or with any other solid. They were able to make a photograph six or eight seconds after a

drop had been placed on a solid and to make subsequent photographs of the same drop at intervals of a few seconds. When the contact angle was measured, the negatives of the photographs, which were 24 × 36 mm in size, were projected on a screen, the image thus being enlarged about 150 times the diameter of the original drop. The contact angle was then determined by drawing a tangent to the point of contact, liquid/solid, and by measuring with a protractor the angle made with the solid by the tangent. Bartell and Merrill (*1*) have employed a similar method in measuring the contact angles of liquids in capillary tubes.

The writer believes that the microprojection of liquid drops in the manner described in the present paper makes possible a simpler and more rapid method for the determination of static contact angle than the methods which have been employed to date.

MICROPROJECTION OF DROP IMAGES

The Principle of the Microprojector.—The apparatus to be described herewith is designated as the "Triple-Purpose Microprojector" (fig. 1), which was designed primarily for the projection of mounted specimens on slides. Images may be projected to a distance of from 4 to 15 feet; the range of magnifications is then from 30-fold to 230-fold. For drawing, however, a mirror reflects the image onto a notebook or sheet of paper directly below it.

A lamp house containing a special 6-volt bulb is adjustably attached to the optical bed of the projector, and the condensing system is attached to the front of the lamp house. For the finer focusing, the objectives are held in a focusing mount operated by a handle traveling in a helical slot; for coarse adjustment, the entire objective holder is moved along the optical bed. This type of adjustment is needed for the accommodation of objects other than microscope slides, the latter being inserted in a fixed position on an object stage rigidly attached to the optical bed in front of the lamp house.

Adaptation of Microprojector for the Projection of Drop Images.—In figure 1 is shown the setup employed for the projection of liquid drops. A cork upon which is glued a platform for glass slides is held in place by a clamp adjustably connected with the vertical rod of a ringstand and placed in front of the object stage, while the objective holder is moved along the optical bed to obtain the proper focus of the image. The object on which the drop is to be placed is put on the platform, which is very easily adjusted into a horizontal position with the aid of a level. In the present investigation, microscope slides were cut into halves lengthwise and, before being placed on the platform, the portion of the

slide to be used was coated with the desired substratum for the drop, such as beeswax, paraffin wax, leaf wax, or scale-insect wax. Also a smooth piece of glabrous leaf, such as the portion between two parallel veins, was sometimes placed on the slide and held in place by thin pieces of glass which were in turn held in place by rubber bands.

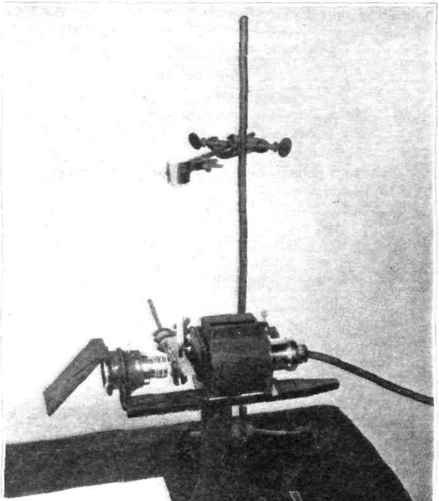

Fig. 1.—Microprojector used to project the images of liquid drops in contact-angle determinations. Description in the text.

In the present investigation, the microprojector was elevated in position by placing it on a box so that the sheet upon which the image was reflected was 34 inches below the mirror; at this distance the image was magnified about 50-fold.

Liquids of high contact angle may be withdrawn from a flask by means of a small pipette, or by means of a splinter of wood tapering to a point about a half millimeter in thickness at one end. Drops with lower contact angle such as oil, or water with reduced surface tension, may be transferred by means of a ruling pen. By touching the substratum with the pen a drop of liquid can be deposited. This can gradually be increased to the desired size by repeatedly touching the same drop with the point of the pen. The volume of liquid given off by the pen can be controlled by a screw regulating the proximity of the spring blades of the pen.

The image may then be traced when the drop has come to rest. The drop outline may be traced or points may be accurately placed on the sharply defined curve outline. The contact angle of the drop will be at its maximum value, for the advancing contact angle is being measured. Evans and Martin (*10*) have shown that it is of little importance whether the advancing or receding equilibrium contact angles are used in comparing wetting agents.

It is convenient to trace the drop outline on cross-section paper, for one of the horizontal lines may then serve as a base for the curve of the drop outline. If the contact angle is to be derived mathematically, it is convenient to place the cross-section or coördinate paper so that one extremity of the curve will rest at the origin of the coördinate axes and the other extremity will rest on the X axis; thus, the coördinate values of different points may be read on the same paper on which the curve is traced.

If the droplet is placed on the substratum on the platform held by the clamp as in figure 1, the temperature in the immediate environment of the drop is about 80° F. Careful observation of the drop image shows that there is no appreciable evaporation of aqueous solution during the time necessary to trace the image. Evaporation of spray oil is, of course, even less rapid. The fact that the temperature is fairly constant, despite minor variations in room temperature, is an advantage in experimental work. Considerable variation in temperature, however, has a very slight effect on contact angle. Du Noüy (*5*, p. 29) states that at around 20° C. each degree of temperature added or substracted corresponds to a difference of only 0.17 dyne in surface tension of an aqueous solution. With more viscous liquids, however, a more remote source of light might be an improvement over the present apparatus in order that heating of the solution above room temperature might be avoided.

MEASUREMENT OF CONTACT ANGLE

Empirical Methods.—Such good definition of the outline of the drop of liquid projected by the microprojector can be obtained that the curve traced on the cross-section paper on which the image of the drop is projected is a very accurate representation of the actual curvature of the drop on the particular substratum in question. Any error in the measurement of the contact angle, therefore, must be that which is inherent in human manipulation. Differences as great as 5½ degrees were noted in measurements made by means of a protractor by various persons independently measuring the contact angle of a single drop outline.

A greater magnification, as obtained by O'Kane *et al.* (*17*) by projecting negatives of the drop images on a screen with a consequent magnification of the original drop of 150-fold, reduces the error of measurement but does not eliminate it, besides having the disadvantage of requiring special apparatus and delay in obtaining the required values.

It appeared to the writer that accurate values could be obtained not from refinements in measuring technique, but from mathematical derivation.

If distilled water is dropped on the surface of a cabbage leaf, the free surface of the water will describe a portion of an ellipse, the shape of which is affected by the side of the leaf upon which the drop happens to be placed (fig. 2, *A* and *B*).

The influence of gravity diminishes as the drop becomes smaller. Even for comparatively large drops (about 5 mm in diameter) the deviation from the spherical shape caused by gravitation becomes less as the contact angle is reduced. As the height of the vertex of the drop becomes less, gravitational effect on configuration of the drop is correspondingly reduced, until when the drop has a contact angle of about 65° (fig. 2, *C*) the effect need not be considered for practical purposes, as will later be shown mathematically.

The drop curvatures dealt with in connection with the present investigation were in every case shown to be exact expressions of ellipse equations. This, in turn, suggested an exact method for the derivation of the contact angle. Since the general equation for the ellipse when its axis is parallel to one of the coördinate axes is $Ax^2 + Bx + Cy^2 + Dy + K = O$, the equation for any given drop curvature may be calculated from the coördinate values of only four points of a curve passing through the origin, from which four simultaneous equations may be derived and four unknowns solved for in terms of the fifth, which may be cancelled out and the resulting figures substituted in the general equation. As

stated before, the coördinate values may be taken directly from the original tracing of the drop outline if it is traced on coördinate paper.

The general equation for the circle is $x^2 + Bx + y^2 + Dy + K = O$. If the curve sufficiently approximates a circle, the coördinate values of only three points are necessary, since only three unknowns need be

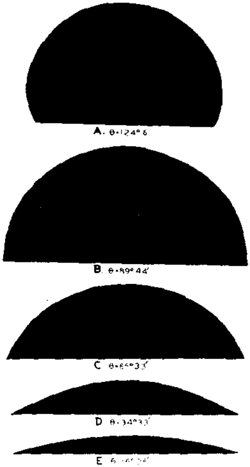

Fig. 2.—Projected outlines of liquid drops. *A*. Water on the ventral surface of a cabbage leaf; *B*, water on the dorsal surface of the same leaf; *C*, water on the dorsal surface of a lemon leaf; *D*, grade 5 (heavy) spray oil on the ventral surface of an orange leaf; *E*, kerosene on the ventral surface of an orange leaf.

solved for. Also, since x^2 and y^2 have no unknown coefficients, the simultaneous equations may be equated to numerical values and the unknowns may be solved for directly.

When the equation of the curve has been computed, differentiation of the equation at $x = O$ will give the slope of the curve at its origin, which is the point of contact, liquid/solid. This value is, of course, the

tangent of the angle of contact, which may then be found by referring to a table of the natural trigonometric functions.

Mack's Formula.—Mack (*15*) has shown that for a drop whose outline is a segment of a sphere, the contact angle may be calculated from the equation $\theta = 2 \tan^{-1}\left(\frac{h}{x}\right)$ where h is the greatest height of the drop and x is the radius of the base of the segment. He states that if it is 0.5 mm or less in diameter, a sessile drop may be considered a segment of a sphere, except for contact angles near 180°. However, it is apparent from inspection of the equations of drop outlines which have been determined by differentiation in the present investigation[6] that for drops as large as 5 mm in diameter, all those having a contact angle less than 65° are for practical purposes segments of spheres. The contact angles of these drops may therefore be calculated by Mack's formula with a great saving of time as compared to the differentiation of the circle equation. Mack's formula was employed in the computation of all the contact angles which are to follow in this paper. By making the drops sufficiently small, say 2 or 3 mm in basal area, even drops with contact angles of around 90° are sufficiently spherical for practical purposes so that Mack's formula may be used in calculating their contact angles.

If reasonably small drops are placed on a solid, a considerable variation in their volumes does not appear to affect their contact-angle values. If too large a drop is placed on a solid, the momentum given to the larger mass of liquid by gravity will cause the contact angle to be reduced to various values within the range of hysteresis. This difficulty may be overcome by waiting until gravitational momentum asserts itself, then building the contact angle up to its maximum value by adding more liquid to the original drop. The independence of contact angle and drop size is in accord with the fact, as Freundlich (*11*) has pointed out, that surface tension remains constant with increase in surface, an important contrast to the tension of a stretching membrane, to which surface tension is sometimes compared.

The writer has found no greater variation in the value θ for liquid

[6] *The equations for the outlines of the drops in figure 2 are for A, B, C, D, and E,* respectively, as follows:

$0.47x^2 - 29.56x + y^2 - 20.15y - 8.08 = 0$; $\Theta = 124°\ 6'$
$0.82x^2 - 58.92x + y^2 + 0.273y - 12.31 = 0$; $\Theta = 89°\ 44'$
$0.98x^2 - 63.33x + y^2 + 28.80y - 31.10 = 0$; $\Theta = 65°\ 33'$
$x^2 - 64.55x + y^2 + 93.93y - 59.87 = 0$; $\Theta = 34°\ 33'$
$x^2 - 62.00x + y^2 + 210.00y - 39.00 = 0$; $\Theta = 16°\ 26'$

As the contact angle changed from 124° 6′ to 65° 33′ the coefficients of x^2 and y^2 became more nearly identical, showing that the ellipse gradually became a circle as the height of the drop diminished with a consequent diminution of the effect of gravity on the shape of the drop.

drops of high contact angle than for those of low contact angle. Thus the θ values for 5 drops of distilled water on beeswax-coated glass slides were found to be 88° 4′, 88° 32′, 89° 16′, 90° 0′, and 87° 34′, an average of 88° 41′ ± 21′. The drops were about 3 mm in diameter. Next 5 drops of grade 4 (medium) spray oil, also about 3 mm in diameter, were placed on a beeswax-coated glass slide and their images projected in the same way as before and under identical conditions (temperature of liquid, 72° C; temperature of air at the point where the drop was placed, 80° C). The computed values for the contact angles were 30° 28′, 31° 56′, 33° 18′, 32° 18′, and 31° 42′, an average of 31° 56′ ± 20′. Approximately the same amount of variation occurred among the 5 measurements in both tests.

A STATISTICAL TEST OF THE RELIABILITY OF THE METHOD

Beeswax surfaces were made by dipping portions of glass microscope slides, made by cutting the standard slide in two parts lengthwise, into melted beeswax at 100° C, after which the slides were placed in a vertical position to cool at room temperatures. This procedure results in a thin, uniform layer of wax on both sides of the glass slides.

TABLE 1

CONTACT ANGLES ON BEESWAX SURFACES OF FIVE DROPS OF ONE-TENTH PER CENT SODIUM OLEATE SOLUTION IN EACH OF FIVE DROP DIMENSIONS*

Width of drops, mm	Drop 1	Drop 2	Drop 3	Drop 4	Drop 5	Mean
1	27° 28′	24° 0′	24° 48′	27° 34′	24° 2′	25° 34′ ± 29′
2	25° 21′	27° 20′	25° 30′	25° 24′	27° 0′	26° 7′ ± 16′
3	26° 45′	28° 4′	27° 56′	27° 44′	27° 22′	27° 30′ ± 8′
4	25° 48′	27° 6′	27° 25′	26° 22′	26° 2′	26° 32′ ± 11′
5	24° 49′	26° 34′	24° 34′	26° 26′	27° 2′	25° 50′ ± 15′

* An analysis of variance revealed no significant differences in contact angle between the various drops of each dimension nor between the drops of different dimensions. However, a comparison of the probable errors shows that the measurements of the drops 3 mm in basal diameter were the least variable.

Drops of 0.1 per cent sodium oleate solution were placed on the beeswax surfaces immediately after the solution had been shaken in the flask. The drops ranged in diameter of basal area from 1 to 5 mm. Five measurements were made of each drop dimension and the contact angles computed from these data by means of Mack's formula. The measurements were made by a laboratory assistant[7] who had no previous experience in this type of work. The resulting figures are shown in table 1.

[7] Mr. Louis Riehl made many of the contact-angle determinations and also aided in the capillarity experiments which are to be mentioned later.

According to an analysis of variance (*19*, p. 22), no significant differences in contact angles were found either between successive measurements of a single drop dimension or between measurements of the five different drop dimensions, although the greatest variation occurred among the latter. This means that the investigator need not concern himself with the exact amount of liquid used to form the drop and that a considerable variation in drop size will not appreciably vitiate results.

TABLE 2

CONTACT ANGLES ON BEESWAX SURFACES OF THREE AQUEOUS SOLUTIONS WITH DIFFERENT WETTING AGENTS*

Material	Approximate width of drop, mm	Contact angle	Mean
Solution A	1	34° 20′	32° 18′ ± 21′
	2	32° 24′	
	3	32° 26′	
	4	31° 20′	
	5	31° 2′	
Solution B	1	41° 10′	40° 54′ ± 19′
	2	40° 48′	
	3	41° 6′	
	4	42° 22′	
	5	39° 6′	
Solution C	1	44° 32′	44° 26′ ± 25′
	2	42° 10′	
	3	46° 28′	
	4	44° 28′	
	5	46° 14′	

* An analysis of variance revealed no significant differences in contact angle between drops of different widths, but showed that the differences between the contact angles of the different solutions were highly significant.

However, a drop size of about 3 mm would probably be chosen as the most convenient size from the standpoint of ease of manipulation, and a variation of over a half millimeter in either direction would not often occur in ordinary work. The probable errors of the means (table 1) show that the least variation occurred among the measurements in the class of drop 3 mm in width and that variation increased in proportion to the deviation from this dimension in either direction. The larger drops tend to flatten out from the force of momentum to reach a contact angle somewhat below the maximum, but, as mentioned before, this difficulty can be overcome by building up the drop by adding more liquid from the ruling pen after the drop has come to rest. The 3-mm dimension, however, appears to be the most convenient and the best suited for the purpose under consideration. As can be seen from table 1, in making

five measurements of drops 3 mm in diameter, one may expect half of the contact-angle values to fall within a range of plus or minus 8 minutes. This represents a far greater accuracy than would be necessary for ordinary purposes.

Measurements were next made of the contact angles on beeswax surfaces of three aqueous solutions with 1 per cent concentrations of different wetting agents (table 2). The wetting agents were Vatsol OT[9] (solution A) and two sulfated alcohols (solutions B and C), differing only in the complexity of the alcohols from which they were derived. An analysis of variance again showed no difference in the contact angles of drops of different dimensions but showed significant differences between the contact angles of different solutions, although the difference between the contact angles of solutions A and B was only 3° 32′ ± 31′.

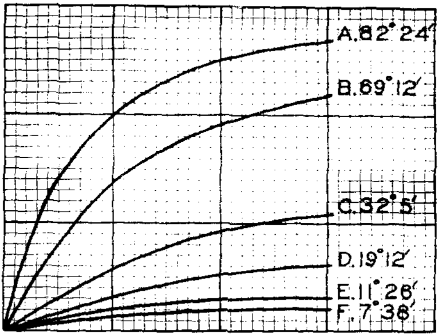

Fig. 3.—Effect of substratum on drop curvature and contact angle of liquids. Each curve shows the contour of the left half of a drop. *A*, Water on the ventral surface of a lemon leaf; *B*, water on the dorsal surface of the same leaf; *C*, grade 5 (heavy) oil on the ventral surface of a *Viburnum* leaf; *D*, grade 5 oil on the dorsal surface of a clean lemon leaf; *E*, grade 5 oil on the dorsal surface of an uncleaned lemon leaf; *F*, grade 5 oil on the dorsal surface of an apple leaf.

SOME CONTACT-ANGLE MEASUREMENTS

Effect of the Nature of the Substratum.—One of the most interesting examples of the effect of the substratum on contact angle is afforded by different leaf surfaces (fig. 3). In his exhaustive study on this subject

[9] Sodium salt of an ester of sulfosuccinic acid.

Stellwaag (*20*) showed that not only does the contact angle of a given liquid vary greatly on leaves from different plant species, but also on leaves of different ages of a single species, or on different surfaces of a single leaf. He also found that desiccation of the leaves had the effect of increasing the contact angle.

The contact angles of both oil and water are higher on young citrus leaves than on older leaves. Also, the contact angles of both oil and water

TABLE 3

VARIATIONS IN THE CONTACT ANGLES OF WATER AND SPRAY OIL ON THE DORSAL AND VENTRAL SURFACES OF THE LEAVES* OF THREE CITRUS VARIETIES

Variety	*Surface of leaf*	*Liquid*†	*Contact angle*‡
Orange	Dorsal	Water	60° 57′ ± 1° 28′
Orange	Ventral	Water	69° 54′ ± 58′
Grapefruit	Dorsal	Water	61° 51′ ± 1° 15′
Grapefruit	Ventral	Water	67° 21′ ± 65′
Lemon	Dorsal	Water	67° 30′ ± 2° 11′
Lemon	Ventral	Water	76° 42′ ± 2° 2′
Lemon (not cleaned)	Dorsal	Water	37° 36′ ± 4° 38′
Lemon (not cleaned)	Ventral	Water	75° 15′ ± 2° 1′
Orange	Dorsal	Oil	27° 58′ ± 59′
Orange	Ventral	Oil	31° 53′ ± 28′
Grapefruit	Dorsal	Oil	21° 20′ ± 40′
Grapefruit	Ventral	Oil	30° 11′ ± 46′
Lemon	Dorsal	Oil	25° 39′ ± 1° 16′
Lemon	Ventral	Oil	28° 32′ ± 53′

* The leaves were all from the second cycle of growth and were consequently of approximately the same age.

† Distilled water and grade 4 (medium) spray oil were used in the test. The temperature of the liquids was 73° F and the temperature of the air at the point where the drop was placed for projection was 80° F. In all tests but one the leaves were washed with tap water and dried with a clean towel before the contact-angle determinations were made.

‡ The differences between the contact angles of the liquids on the dorsal and ventral sides of each leaf were significant.

are greater on the ventral sides of citrus leaves of the second growth cycle than on the dorsal (upper) sides (table 3). Thus a spray solution will roll into beads on the ventral sides of citrus leaves, while the same solution may wet the leaf in an even film on the dorsal side of the same leaf. The spray solution will also "bead" more on younger leaves than on older leaves. The probable errors in table 3 show that, with a single exception, the contact angles of both the water and oil drops are more variable on the dorsal than on the ventral sides of the leaves.

Table 3 shows that the contact angle of water on the ventral sides of citrus leaves is higher than on the dorsal sides; it does not seem, however, that the differences which were found on clean leaves are in proportion to the great differences between the spreading of spray solutions on the dorsal and ventral sides of citrus leaves which may be observed

when spraying trees. Under actual field conditions the dorsal sides of the leaves have a layer of orchard dust, while the ventral sides have practically none. Since water spreads well on a layer of soil particles, the dorsal sides of the leaves are readily wetted. The test (table 3) in which the leaves were not washed showed that on leaves as they occur in the orchard, the differences in the contact angles of water on the dorsal and ventral sides of the leaves are much greater than on clean leaves.

As stated before, a uniform substratum may be obtained by dipping a microscope slide into melted wax and keeping the slide in a vertical position while the coating of wax is cooling, or by dipping the slide into

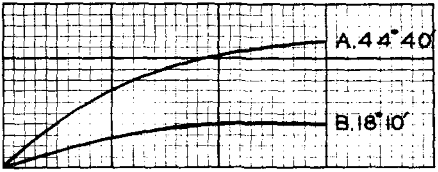

Fig. 4.—The drop curvatures and contact angles of grade 5 (heavy) spray oil on extracted leaf wax (*A*) and extracted red-scale wax (*B*).

a solution of wax and carbon tetrachloride (25 per cent wax and 75 per cent carbon tetrachloride) and placing the slide in a vertical position while the carbon tetrachloride is evaporating. In the present investigation comparisons are being made of the contact angles of various liquids on uniform surfaces of paraffin wax or beeswax. Since it was considered that a knowledge of the preferential wetting of oil with respect to citrus-leaf wax and the wax of red scale, *Aonidiella aurantii* (Mask.), would be at least of academic interest, these waxes were extracted by soaking the scales and leaves in petroleum ether for five days with occasional shaking of the solution. The scales or leaves were then removed and the ether driven off by heat.

Figure 4 shows that the contact angle of oil is much lower on scale wax than on leaf wax. However, the extract from the entire scale body may not be representative of the waxy threads exuded by the insect which comprise the mass of wax beneath the scale body through which the oil must penetrate in order to reach the spiracles.

That the oil can traverse the comparatively great distance from the margin of the scale body to the spiracles before penetrating the cuticle

of the leaf is not surprising in view of the fact that the wax on the underside of the scale body, which must be traversed by the oil on its way to the spiracles, is made up of a mass of loosely woven, waxy threads exuded by glands on the pygidium of the insect (fig. 5). In this way a great surface area per unit distance is presented to the oil, with a consequent increase in the capillary attraction. If a red scale is fixed securely on its dorsal surface, as by placing it on a thin layer of balsam, and a

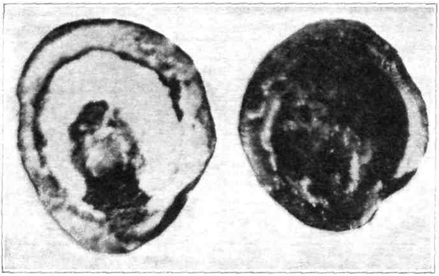

Fig. 5.—Red scales removed from a lemon leaf, each placed on its dorsal side to show the ventral mass of waxy threads between the scale body and its substratum. The scale on the right was sprayed with oil, which penetrated through the mass of wax into the spiracles of the insect and consequently caused the wax to become translucent, revealing the dark body of the scale. Greatly magnified.

small drop of oil is placed on the center of its ventral surface, the oil will spread rapidly to the edges of the scale, while a drop of similar size placed on the dorsal side of a scale will spread much more slowly.

The capillary nature of the mass of wax beneath the body of the red scale (fig. 5) favors the rapid penetration of oil to the spiracles of the insect. If sufficient oil is deposited by the spray, the oil reaches the spiracles in an instant, which proves that the movement of oil to the spiracles is by capillary flow, for if the movement of oil were by penetration of solid wax, several days, at least, would be required for penetration to the spiracles. In fact, the oil would be absorbed by the substratum upon which the scale happened to be situated before it could reach the relatively long distance from the edge of the scale armor to the spiracles, which are situated at points about two-thirds the distance from the edge of the scale armor to the center of the insect.

If the scale is situated on a highly absorptive substance, such as the rough bark of citrus trees, the oil may penetrate this substance before it reaches the spiracles of the scale, despite the fact that it penetrates under the scale so readily. Consequently, greater concentrations of oil in the spray are necessary to insure the penetration of the oil to the insect spiracles.

A knowledge of the contact angle of oil on water was considered desirable in view of the fact that it is commonly conceived that each drop of water as it strikes the tree surface in the spraying operation bears on its surface numerous small lenses of oil (*18*, p. 60). This, of course, is not true of the emulsive oils, which spread in a thin film over water.

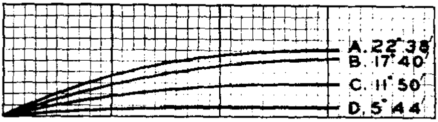

Fig. 6.—Outlines and contact angles of drops of spray oil on water. *A*, Heavy oil (U. R. 95); *B*, light-medium oil (U. R. 92); *C*, light-medium oil (U. R. 80); *D*, light-medium oil (U. R. 92) with 1 per cent glyceryl monoöleate.

A thin film of water without sufficient slope or contour to cause movement of an oil drop placed upon it may be obtained by cleaning to absolute chemical cleanness a strip of glass, such as used in the present investigation to hold in place the strips of leaves. The glass is then covered with distilled water and placed on the slide platform in front of the microprojector objective. A drop of oil may then be placed on the water, upon which it will form a lens (fig. 6). Oils low in U. R. (unsulfonatable residue) and oils containing a surface-active solute such as glyceryl monoöleate were shown to have a lower contact angle on water than pure saturated oil, as figure 6 shows.

Tests with Various Solutes.—Proteins, saponin, soaps, sulfite lyes, alkyl sulfates, alkyl sulfonates, Igepons, petroleum sulfonic acids, and organic acid derivatives were tested with regard to their effect on the contact angle of water on various surfaces. A few preliminary tests resulted in the following values for the contact angle of distilled water alone and distilled water with various solutes on the ventral surfaces of *Viburnum* leaves: water alone, 70° 18′; water with 1 per cent ethyl alcohol, 54° 14′; with 0.01 per cent Vatsol OT, 45° 22′; with 0.1 per cent sodium oleate, 42° 26′; with 0.05 per cent sulfated alcohol or 0.5 per cent dry blood albumin spreader, 38° 50′; with 0.5 per cent Castile soap,

36° 1′; with 0.1 per cent Vatsol OT, 30° 14′; and with 1.0 per cent Vatsol OT, 27° 57′. The greatest reduction in contact angle per unit concentration was obtained with Vatsol OT. On *Viburnum* the compound practically reaches its maximum effect at 0.1 per cent concentration, although on beeswax a reduction in contact angle of 11° 41′ (from 45° 9′ to 33° 28′) was effected by increasing the solute from 0.1 per cent to 1.0 per cent concentration.

While Vatsol OT, 0.1 per cent, proved to be more effective than sodium oleate, 0.1 per cent, in reducing the contact angle of water on *Viburnum* leaves, it was less effective than sodium oleate on a beeswax

TABLE 4

THE RELATIVE SPREADING ABILITY OF SOLUTIONS OF VATSOL OT AND SODIUM OLEATE ON BEESWAX AND *Viburnum* LEAVES AS SHOWN BY CONTACT-ANGLE MEASUREMENTS

Solution*	Substratum	Contact angle
Vatsol OT	Beeswax	43° 19′ ± 31′
Sodium oleate	Beeswax	31° 34′ ± 15′
Vatsol OT	Leaf A	29° 42′ ± 46′
Vatsol OT	Leaf B	30° 14′ ± 40′
Sodium oleate	Leaf A	39° 6′ ± 36′
Sodium oleate	Leaf B	42° 43′ ± 33′

* Concentrations of both solutes were 0.1 gram per 100 cc distilled water. The temperature immediately surrounding the drops was 80° F.

surface, as can be seen in table 4. This interesting observation indicates that chemical relations play a rôle in wetting and spreading as well as do purely physical factors. If only physical factors were involved, it would be expected that the chemical compositions of the solutions or the solid substrata would affect the degree of wetting and spreading as far as they affected free surface energy, but that the difference between the contact angles of two solutions on one substratum would be in the same direction, if not in the same degree, on another substratum. The present test shows that this may not always be the case.

In table 5 are given the contact angles on beeswax surfaces of aqueous solutions with various percentages of seven different wetting and spreading agents. Of special interest in this table is the superior effectiveness of sodium oleate as a wetting agent on beeswax; also, the maximum reduction of contact angle was reached at a concentration of 0.05 per cent or possibly somewhat lower, and from this point on the efficiency of the soap decreased as the concentration increased. The same situation obtains to some extent with regard to the sulfated alcohol IN–181.

If either red scale or black scale, *Saissetia oleae* (Bern.), are removed

from a leaf and covered with a solution of 0.1 gram Vatsol OT per 100 cc water, the solution will quickly penetrate for varying distances into the tracheae. The extent of penetration of the liquid into the tracheae can be determined because of the change in refractive index of the contents of the tracheal tubes caused by the entrance of the liquid, which makes them appear lighter in color (*4*). The line of demarcation between the air-filled and the liquid-filled portion of a tracheal tube is very distinct.

TABLE 5

CONTACT ANGLES ON BEESWAX OF AQUEOUS SOLUTIONS WITH VARIOUS SOLUTES, AT FIVE DIFFERENT CONCENTRATIONS*

Solute	Per cent concentration				
	0.01	0.05	0.1	0.5	1.0
Vatsol OT†	78° 14′ ± 42′	50° 34′ ± 28′	45° 9′ ± 39′	36° 4′ ± 37′	33° 28′ ± 18′
Vatsol OTC	81° 12′ ± 36′	80° 15′ ± 24′	75° 28′ ± 54′	63° 7′ ± 42′	50° 27′ ± 20′
Vatsol OT (aqueous)	84° 30′ ± 21′	79° 48′ ± 25′	73° 30′ ± 93′	60° 4′ ± 60′	49° 25′ ± 27′
Tergitol No. 7‡	75° 54′ ± 23′	71° 30′ ± 27′	65° 0′ ± 54′	38° 24′ ± 28′	35° 54′ ± 26′
1N-181§	67° 11′ ± 63′	45° 54′ ± 57′	46° 54′ ± 52′	49° 54′ ± 45′	48° 54′ ± 29′
Aresket¶	80° 24′ ± 74′	71° 23′ ± 35′	59° 54′ ± 105′	51° 0′ ± 16′	49° 42′ ± 25′
Sodium oleate	57° 18′ ± 75′	27° 12′ ± 21′	27° 27′ ± 11′	20° 2′ ± 34′	32° 17′ ± 32′

* Each figure is the average of five tests. The temperature immediately surrounding the drop was 80° F.

† Sodium salt of an ester of sulfosuccinic acid.

‡ Sulfated higher alcohol.

§ Sodium lauryl sulfate.

¶ Sodium salt of an alkylated aryl compound.

Wilcoxon and Hartzell (*22*) found that a water solution of 0.5 per cent sodium oleate which penetrated one third to two thirds the length of the tracheae of the larvae of tomato worms (*Phlegethontius quinquemaculata*) was not able to penetrate the tracheae at all after the larvae were killed with HCN. These investigators believed that respiratory movements, or at least vital activity, are necessary to make possible the penetration of this solution into the tracheae. In the present investigation, however, red scale were killed with HCN, and the tracheae of these insects were as readily penetrated by solutions of 0.5 per cent sodium oleate or 0.1 per cent Vatsol OT as were the tracheae of living insects. It is doubtful whether the structurally degenerate red scales have sufficient respiratory or vital activity to influence the penetration of liquids into their tracheae; but, on the other hand, since the tracheal tubes are smaller in diameter than those of the tomato worm, they may be more readily penetrated by means of capillary action, and the liquids may flow a greater distance into the tubes after entering the spiracles.

RELATION OF SURFACE TENSION AND CONTACT ANGLE TO PENETRATION DIFFERENTIAL

Mathematical Considerations.—Hoskins (*13*), neglecting hydrostatic pressure, has expressed the linear rate of flow of a liquid in capillary tubes as:

$$f = \frac{\gamma \cos \theta \, r}{4\eta l}$$

in which γ is the surface tension of the liquid, θ the contact angle, r the radius of the tube, η the viscosity of the liquid, and l the distance penetrated. It should be pointed out that this equation holds only for a condition *far from equilibrium*; *the presence of r in the numerator of the* fraction is thus explained.

If there were no more than two variables in the equation above, a differential form of the equation could be integrated to obtain an equation for total length of flow. The variable $\cos \theta$ might be ignored, as Hoskins (*13*) suggests, for situations in which the contact angle is zero or nearly so; but for the purposes of the present investigation reference will be made to the well-known formula for height of capillary rise of a liquid:

$$h = \frac{2\gamma \cos \theta}{rg}$$

An inspection of the formulas given above will show that a reduction in surface tension will invariably decrease the rate or distance of penetration only if the contact angle of the liquid on the inner surface of the capillary tube is zero or sufficiently small so that further decrease in the angle will not result in any important changes in the value $\cos \theta$. If the contact angle of the liquid on the sides of the capillary tube is high, however, as in the case of water in a waxy capillary tube, a decrease in γ results in a decrease in θ and a corresponding increase in $\cos \theta$, so that the value $\gamma \cos \theta$ may be actually increased by reduction in surface tension, with a consequent increase in the rate and distance of penetration of the liquid. An increase in the value $\gamma \cos \theta$ can occur only if the rate of increase of $\cos \theta$ is greater than the rate of decrease of γ. This will later be shown by actual experiment to be what happens.

If an insect, which is wetted with difficulty, is located on rough, porous bark, the spray liquid may penetrate into the bark so rapidly that insufficient liquid remains on the surface to wet the insect, to penetrate into waxy barriers as in the case of the woolly aphid or egg masses, or to penetrate under the bodies of sessile scale insects to the spiracles or regions in which the spray can exert its maximum insecticidal effect. A good example of this disadvantageous penetration differential is the

case of oil sprays applied against the California red scale. The thin film of oil applied to the branches upon which the scales rest is absorbed by the bark so rapidly that it often does not have sufficient time to penetrate the waxy mass (fig. 5) under the scale, which blocks the way of the oil to the spiracles. Consequently, with a given concentration of oil in the spray, nearly all adult red scale may be killed on the leaves, green twigs, and fruit; while perhaps only 60 or 70 per cent may be killed on the larger branches.

Experiments with Water and Aqueous Solutions.—Since the contact angle of water on chemically clean glass is zero, and since glass is transparent, glass tubes offer an excellent means of studying the effect of changes in surface tension on the capillary flow of water. Likewise the inner wall of a glass tube may be coated with a layer of wax so thin as not to interfere greatly with the visibility of the liquid column, yet capable of increasing the contact angle of the liquid to 90°. The same capillary tube may thus serve to demonstrate the effect of changes in surface tension on capillary flow in the one case where contact angle is eliminated as a variable affecting capillary flow and in the other case in which contact angle is an important factor.

Absolute cleanliness is essential in experimental work such as suggested above. On the other hand, if the cleaned glass can be kept in a container with clean air, the matter of air adsorption is probably not of as great importance as many investigators have considered it. Edser (*8*) states that Rayleigh has proved that when glass has been heated in a smokeless flame, water spreads over it readily (implying a zero contact angle), even after the surface has been exposed to pure air for several days. On the other hand, Edser (*8*) states that, ordinarily, greasy matter will be deposited on glass from the air, in which case water will no longer have a zero contact angle on the glass.

In an experiment involving the use of glass capillaries some 1-mm capillary tubing was cut into sections 4 inches long. A mark was made with a file ¼ of an inch from one end of each tube. The tubes were immersed up to this mark in the liquid to be tested. Four tubes were used in each series of tests and these were then cleaned again and used for another series of tests.

All four tubes were placed in a bath of chromic acid and left from one to several hours. From the chromic-acid bath the tubes were placed in a bath of concentrated nitric acid and left for 2 minutes, then rinsed to remove the acid. The tubes were then rinsed in double-distilled water for 2 minutes. They were then placed in a bath of caustic potash for 2 minutes and rinsed in this solution. After this they were again rinsed

in double-distilled water, the water being changed for each successive tube.

The tubes were dried by means of an air stream taken from a pressure line supplied to the laboratory table. The air was first bubbled through chromic acid to remove organic matter, then bubbled through a distilled water bath, and afterwards passed through a bottle loosely filled with glass wool to prevent excess moisture from being carried into the drying towers. The air was passed through two drying towers, the first containing calcium chloride and the second barium perchlorate. Glass wool

TABLE 6
DIFFERENCES IN CAPILLARY FLOW OF WATER IN CLEAN-GLASS AND WAXED-GLASS CAPILLARY TUBES CAUSED BY REDUCTION OF SURFACE TENSION

Inner wall of tube	Concentration of solute (Vatsol OT), per cent	Surface tension of liquid, dynes per cm*	Height of liquid column, cm*
Glass	None	72.7 ± 0.01	2.12 ± 0.09
	0.1	32.1 ± .09	0.85 ± .02
	1.0	29.1 ± .01	0.72 ± .02
Beeswax	None	72.7 ± .01	0.00
	0.1	32.1 ± .09	0.39 ± .03
	1.0	29.1 ± 0.01	0.65 ± 0.02

* Average value for five tests.

was placed at the entrance and exit of each drying tower to prevent the carrying of dust in the air stream from the drying towers.

The air was passed through a glass tube 10 inches long and ¾ inch in diameter. This tube was heated by means of a Fischer burner so that the air might be heated sufficiently to prevent the deposition of any moisture it might contain on the walls of the capillary tubes which were to be dried. A cork containing a hole of just the right size for the capillary tube to fit in firmly was placed at the distal end of the large glass tube and the stream of heated air was passed through the capillary tube to dry it. The air stream was directed through the tube for 3 minutes.

The capillary tube was then placed in a desiccator for 5 minutes to allow it to cool. After this it was placed on a stand constructed so that the tube might be held in place with the file mark at the lower end of the tube directly at the surface of the liquid to be tested. Each tube was left in the liquid 5 minutes before the column of water was measured.

A ring fashioned from a soft metal band was placed around each tube before it was placed in the solution being tested. The column of liquid

in the tube was measured by sliding the metal ring until its bottom edge coincided with the bottom of the liquid meniscus. The tube was then removed from the liquid and the distance from the file mark near the bottom of the tube to the bottom of the metal ring was then measured with a micrometer caliper.

To obtain the wax coating, a capillary tube 16 inches in length and of the same diameter as the tube previously mentioned was used. A 25

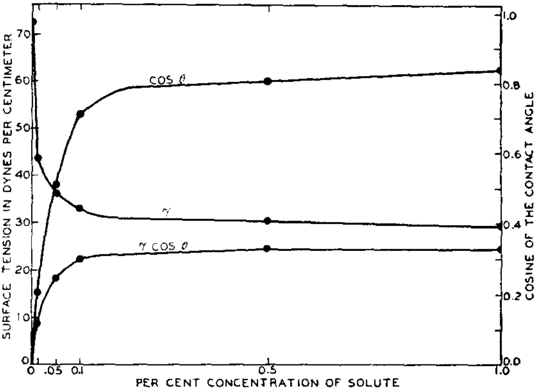

Fig. 7.—Changes in surface tension of water, cosine of the contact angle of water on beeswax, and the product of these two factors, with increasing concentration of Vatsol OT. Compare with curves for capillary flow of liquids shown in figure 8.

per cent solution of beeswax in carbon tetrachloride was drawn into the tube and allowed to drain out. The carbon tetrachloride was evaporated by passing air through the tube. The tube was then cut into four sections 4 inches in length, as before. The height of the column of liquid to be tested was measured in the same way as in the previous tests. Vatsol OT was used as the solute to reduce surface tension, and in the present experiment, as well as subsequent experiments, the solutions were one hour old at the beginning of the tests. However, the flasks containing the solutions were shaken before each test. Determination by means of an Ostwald viscometer showed that in the case of the aqueous solutions the solute had no appreciable effect on viscosity. The experiment was

made at a temperature of 72° F, which was also the temperature of the solutions. The results of the experiment are presented in table 6, and show that a given reduction in surface tension caused an increased penetration in the waxed tubes and a reduced penetration in the clean glass tubes. Thus a penetration differential was effected by the addition of a solute.

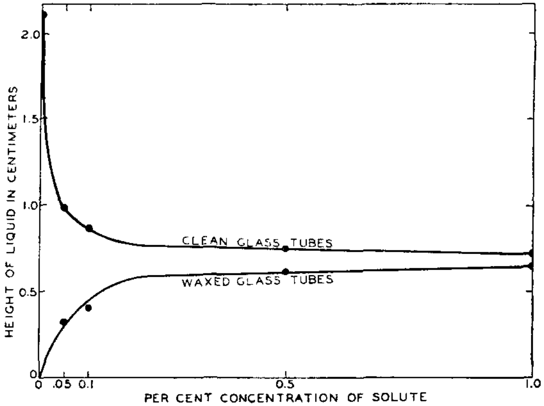

Fig. 8.—Changes in the penetrativity of water in clean glass tubes and waxed glass tubes with increasing concentration of Vatsol OT as determined by experiment. Compare with theoretical expectations as shown in figure 7.

Figure 7 shows graphically the relation of surface tension, the cosine of the contact angle, and the product of these two factors as the concentration of Vatsol OT is increased from 0 to 1.0 per cent. Figure 8, which presents graphically the data in table 6, shows the relation of concentration of solute and, consequently, reduction in surface tension to penetration. The curves for penetration in a clean glass tube and in a waxed tube (fig. 8) are, respectively, rather similar to the curves for surface tension and the product of surface tension and cosine of the contact angle (fig. 7), which is consistent with theoretical expectations.

Data similar to those given above were obtained by using columns of sand as the capillaries. As in all experiments to be mentioned subsequently, the experiment was made at room temperature. Quartz sand of

20-mesh size and less was cleaned by washing in a chromic-acid solution, repeatedly rinsing with distilled water until all traces of chromic acid were removed, and then drying in a flask over a flame and cooling. The sand was then poured into ½-inch glass tubes a foot in length. Another portion of the cleaned sand was immersed in carbon tetrachloride containing 25 per cent paraffin wax. The solvent was evaporated and the sand was sieved through a 20-mesh screen and poured into glass tubes as before. Three tubes with clean sand were placed with their lower ends immersed in water and Vatsol solution: one in pure distilled water, one in a 0.1 per cent Vatsol solution, and one in a 1.0 per cent Vatsol solution. This procedure was repeated with the tubes of waxed sand. For some reason the differences were not so great as those found in connection with the glass capillary experiment (table 6), but they were in the same direction. In the columns of pure sand, in 15 minutes the pure water had risen 10.8 cm; 0.1 per cent Vatsol solution, 9.7 cm; and 1.0 per cent Vatsol solution, 9.2 cm. The corresponding distances of penetration in 16 hours were, respectively, 17.4 cm, 16.1 cm, and 13.7 cm. In the columns of waxed sand in 15 minutes the pure water had not risen a discernible distance, the 0.1 per cent Vatsol solution had risen to a height of 0.4 cm, and the 1.0 per cent solution had risen to a height of 3.1 cm. The corresponding distances in 16 hours were, respectively, 0.2 cm, 0.8 cm, and 3.7 cm.

Some smoothly planed Douglas fir boards were used to test the rate of penetration of water and 1.0 per cent Vatsol solution into wood, on which the contact angle of water is comparatively low. In five separate tests 1 cc of distilled water was placed in a glass cylinder 1 cm in diameter and 4 cm long; this was glued to the board in a vertical position with a commercial waterproof glue, and 4 inches away a similar cylinder was attached in which 1 cc of a 1.0 per cent Vatsol solution was poured. In the five tests, in only one case was the rate of penetration of the Vatsol solution greater than that of the pure water, the average time for the disappearance of the 1 cc of liquid being 55 hours for the pure water and 63 hours for the Vatsol solution.

When the rates of penetration of pure water and a 1.0 per cent Vatsol solution were compared on a board of a commercial pressed fiberboard of Douglas fir wood with a density of 18 pounds per cubic foot, it was found that 3 days were required for the penetration of 1 cc of water and only 20 seconds for the penetration of the Vatsol solution. In this case the penetration was a surface rather than a capillary phenomenon. The layers of wood fiber are so loosely packed that penetration through the mass depends upon the ability of a liquid to spread along a surface.

Since water has an appreciable contact angle on resinous wood, the Vatsol solution spreads much more rapidly on a level surface than pure water and consequently enters a loose mass of wood fibers much more rapidly. This does not mean that the Vatsol solution will enter a more solid mass of wood fibers, in which capillarity is involved, more rapidly, for just the opposite was shown to be the case, as the data for penetration of water into the seasoned Douglas fir lumber show. The effect of surface tension on speed of penetration is then shown to be not only affected by contact angle in the medium penetrated, but is also affected

TABLE 7

DIFFERENCES IN DISTANCES OF FLOW OF WATER IN COLUMNS OF CITRUS-BARK FRAGMENTS CAUSED BY REDUCTION OF SURFACE TENSION

Concentration of solute (Vatsol OT), per cent	Surface tension, dynes per cm	Condition of bark fragments	Distance (cm) of penetration in:		
			1 hour	4 hours	16 hours
None	72.7	Loosely packed	....	....	10.6
1.0	29.1	Loosely packed	....	....	8.9
None	72.7	Moderately packed	....	....	20.0
1.0	29.1	Moderately packed	....	....	13.5
None	72.7	Tightly packed	4.5	9.3	12.0*
1.0	29.1	Tightly packed	1.8	2.0	2.4

* Liquid reached upper limit of column.

by the density of the medium penetrated. If the density of the medium to be penetrated falls below a certain point, the rate of flow may no longer be affected by laws of capillarity, but by the laws of open surface flow in which reduction in surface tension invariably results in more rapid spread of a liquid.

Owing to the great variability in the rate of penetration of water solutions in Douglas fir wood, the method described above was not considered satisfactory as a means of comparing the penetrativity of different solutions. To standardize the capillary medium, fragments of bark were tamped into ½-cm glass tubes in equivalent amounts and in a uniform standard manner and the flow of liquid up into these columns of bark fragments was determined. The bark fragments were made by filing the outer bark off dry orange limbs 2 or 3 inches in diameter. It is this outer bark with which the investigator is concerned in the penetration of films of water or oil when spraying for certain citrus pests.

The results of three tests are summarized in table 7. The data show that in every test a reduction in surface tension of the water retarded

its distance of penetration into the columns of bark fragments. This is to be expected in view of the relatively low contact angle of water on citrus bark. The data likewise show that the more tightly packed the bark fragments are, that is, the more truly the flow of liquid is a capillary phenomenon as opposed to surface-flow phenomena, the greater is the difference in the distance penetrated, between pure water and water with solute. This difference was, however, more definitely emphasized in the great contrast in the ratios of the rates of disappearance of 1-cc portions of water and Vatsol solution in natural Douglas fir wood and the loosely pressed pulp, concerning which the data have been previously given.

The greater penetrativity of pure water than that of Vatsol solution in citrus bark is of special interest since it has been shown that water will not enter under the armor of the California red scale unless its surface tension is greatly reduced. The matted threads of wax (fig. 5) under the body of the red scale make a waxy capillary system, as has been mentioned before. On this wax the contact angle of water is high, whereas on wood it is relatively low. Obviously, reduction in surface tension must reduce the penetration differential of water flowing in wood and scale wax, just as it does in the case of water flowing in glass and wax capillaries (fig. 8).

Experiments with Spray Oil.—Unfortunately it is difficult to reduce the surface tension of spray oil. The surface tension is already so low that very few solutes are sufficiently surface-active in oil to reduce its surface tension more than an unappreciable amount. Pertinent in this regard also are the observations of Langmuir and Harkins (see Clark, *3*, p. 324) that the surface energy of liquids is determined principally by the structure of the surface layer of atomic groupings. The liquid hydrocarbons have methyl groups at the ends of their chains; consequently the surface energies of different compounds are approximately equal and are independent of the length of the chain. Even the alcohols possess about the same surface energy as hydrocarbons because the methyl groups are on the surface, with the polar hydroxyl groups pointing inward.

Glyceryl monoöleate, which is so effective in retarding the penetration of oil into waxy substances such as leaf cuticles because of the polarity given it by its hydroxyl radicals (*7*), has no effect in decreasing the penetration of oil into porous bark because in this case the penetration is a capillary phenomenon, and the glyceryl monoöleate, having no effect on the surface tension or the viscosity of the oil, has no effect on the penetration of the oil into capillary tubes, regardless of the chemical composition of the tubes. This is obvious from an inspection of the

formulas for capillary flow. However, tests were made to demonstrate this point.

In an experiment in which 1-mm glass capillaries were cleaned and coated with beeswax in the same manner as described before with regard to the experiments with aqueous solutions, the height to which columns of oil with and without 1 per cent glyceryl monoöleate ascended in the capillaries was observed and recorded. Each figure given below is the average of five measurements of the distance reached by the column of oil. In the clean glass capillaries, a grade 3 (light-medium) oil rose to a height of 1.03 ± 0.05 cm, and the same oil with 1 per cent glyceryl monoöleate rose to a height of 1.00 ± 0.05 cm; the corresponding figures for the rise of the oils in the waxed capillaries were, respectively, 1.40 ± 0.07 cm, and 1.36 ± 0.03 cm. The addition of glyceryl monoöleate caused no significant difference in the heights of the columns of oil in either the clean glass or the waxed capillaries.

SOME INSECTICIDAL TESTS WITH AQUEOUS SOLUTIONS

The penetration of oil under the body of a red scale (fig. 5) appears to be a prerequisite to lethal effect (*6*). This, in turn, suggested that if toxic aqueous solutions could be made to penetrate under the scale insect's body, they might result in death to the insect either by tracheal penetration, or, if the spiracles were not reached, by penetration of the ventral covering (*6*) of the insect. The possibility of the latter action is enhanced by the fact that once the liquid has penetrated the waxy margin of the insect and is under the body, it is practically unaffected by evaporation. On the exposed portions of an insect an aqueous solution is quickly removed by evaporation.

The contact-angle measurements of aqueous solutions with various solutes served as a valuable guide in the search for liquids with maximum spreading ability on waxy surfaces. Certain organic acid derivatives proved to be especially effective in reducing the contact angle of water on leaves and other waxy surfaces. Water containing these solutes above a certain concentration was able to penetrate the waxy margins of the scales and flow under their bodies. Concentrations of other wetting agents far beyond any amounts that would be practical in commercial usage were not sufficient to produce this effect.

The waxy layer (fig. 5) between the body of a red scale and its substratum (fruit, leaves, bark, etc.) is not homogeneous, but comprises a mass of rather loosely woven threads of wax exuded from the pygidium of the insect (*6*). If the contact angle of an aqueous solution is suffi-

ciently reduced, the solution is able to flow through this mat of waxy threads in much the same manner as oil; yet it has an advantage over oil, for being an aqueous solution it does not have the wax-dissolving properties of oil and consequently does not soak through the waxy cuticle of the leaves, except perhaps to an unappreciable extent. Aqueous solutions may have the spreading properties of oil without the ability of oil to penetrate solid wax. For this reason toxic materials injurious to plants put in aqueous solutions in concentrations sufficient to cause death of insects with safety to the plant would cause serious injury to the plant when put in oil and applied in a dilute oil spray.

In his attempts to find a nicotine spray which would be satisfactory for use against the woolly aphid, *Eriosoma lanigerum* (Hausm.), Greenslade (*12*) had a problem similar to the one encountered in attempting to make aqueous solutions kill red scale. He found that the aphids were killed by a 0.025 per cent concentration of nicotine if the spray liquid actually reached the bodies of the insects, but that it was difficult to wet and penetrate the mass of wax threads which cover each insect and become interlaced over the top of the colony. The effectiveness of the spray against the aphids was so closely correlated with spreading ability that Greenslade used the percentage of kill as a criterion of spreading power. With a 0.025 per cent nicotine solution the per cent kill increased from 1 to 96.6 as the per cent concentration of a soft-soap solution was increased from 0.1 to 3.0 (fig. 9).

The penetration of aqueous solutions under a red scale's body may be demonstrated by coloring the solution with a dye, such as saure fuchsin. Although not enough dye is carried under the insect's body to give a general colored appearance, yet where irregularities of the body occur, such as body segments or fragments of wax, an accumulation of dye occurs and can readily be seen with the aid of the low-power objective of the microscope.

Often when adult red-scale females are dislodged from a fruit, one or more newly emerged larvae ("crawlers") may be seen under the armor in the region of the pygidium. The toxic aqueous solutions which were tried with 0.1 per cent Vatsol OT flowed under the scale armor and killed these crawlers. If the same solution is used with 0.05 per cent Vatsol OT, an occasional crawler may be found alive, while if only 0.01 per cent Vatsol OT is added to the solution, it does not have the ability to spread under the scale armor to any great extent and consequently the majority of crawlers are not reached by the solution and may be seen crawling about actively when the scale is turned on its ventral side and examined with a microscope. As has been stated previously, 0.01 per

cent Vatsol OT has about the same effect in reducing the contact angle of water on a leaf surface as 0.5 per cent sulfated alcohol or 0.5 per cent sodium oleate. A solution may give a complete wetting of a surface without having the ability to penetrate under the scale armor. For example, if twice as much blood albumin spreader as is ordinarily used in commercial spraying (8 ounces per 100 gallons of water) is placed in an

TABLE 8

THE INFLUENCE OF THE WETTING AGENT ON THE EFFICACY OF AQUEOUS SOLUTIONS OF SODIUM DINITRO-O-CYCLOHEXYLPHENATE AGAINST CALIFORNIA RED SCALE

Test no.	Concentration of toxicant, per cent	Wetting agent	Concentration of wetting agent, per cent	Number of insects counted*	Net mortality,† per cent
1	0.1	Vatsol OT	0.025	2,141	21.2 ± 0.73
2	0.1	Vatsol OT	0.05	1,872	57.3 ± 0.94
3	0.1	Vatsol OT	0.1	3,306	73.6 ± 0.53
4	0.1‡	Vatsol OT	0.1	2,348	83.2 ± 0.63
5	0.1	Vatsol OT	1.0	3,447	80.7 ± 0.55
6	0.2	Vatsol OT	1.0	2,313	84.8 ± 0.61
7	0.5	Vatsol OT	1.0	1,783	99.5 ± 0.14
8	0.1	Tergitol	0.1	3,416	32.7 ± 0.67
9	0.05	Tergitol	1.0	2,731	69.2 ± 0.73
10	0.1	Tergitol	1.0	2,249	78.6 ± 0.84
11	0.1	Blood albumin	0.03	1,237	0.0
12	0.1	Blood albumin	0.3	1,825	46.6 ± 0.96
13	0.1	None	...	946	0.0
14	0.0	Vatsol OT	1.0	1,362	0.0
15	0.0	Tergitol	1.0	1,573	0.0

* There were 4,741 insects in the control, of which 66.2 per cent were alive.

† Calculated as $\frac{x-y}{x}$ when x = percentage left alive in untreated lot and y = percentage left alive in treated lot. Probable error computed from the formula $P.E. = 0.6745\sqrt{\frac{pq}{n-d}}$, when p = net per cent mortality; $q = 100 -$ net per cent mortality; n = number of insects counted; and d = number of n which would have died from natural causes during the course of the experiment as determined by the percentage of dead insects in the check.

‡ The toxicant was dissolved in acetone and the acetone solution was used at 1.0 per cent concentration.

aqueous solution sufficiently toxic to kill the crawlers which happen to be located under the armor of a scale, none of the crawlers will be killed by the solution, even though a uniform wetting of the surface of the scale-infested fruit is obtained. If a more effective spreading agent is added to the solution containing the blood albumin, it will flow under the scale armor and kill the crawlers and the adult insect also, provided the aqueous solution is sufficiently toxic.

Data on the insecticidal effect of a compound known as dinitro-o-cyclohexylphenol were first published by Kagy and Richardson (*14*), who dissolved the compound in oil. In the present investigation, dinitro-o-cyclohexylphenol was used in aqueous solutions in the form of a so-

dium salt. Kagy[8] had already determined the merits of this particular salt of dinitro-o-cyclohexylphenol as well as other salts of the same compound as early as 1931.

The test insects were California red scale infesting grapefruit. Counts were made on adult and gray-adult (6) insects only. The scale-infested fruits were dipped in the toxic solutions and kept at a temperature of

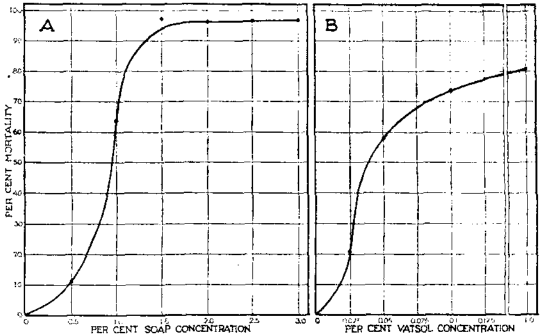

Fig. 9.—The effect of the addition of spreader to contact sprays on their effectiveness against insects protected by waxy barriers. *A*, Mortality curve of woolly aphid with increasing concentrations of soap in a nicotine solution (after Greenslade). *B*, Mortality curve of red scale with increasing concentrations of Vatsol OT in a sodium dinitro-o-cyclohexylphenate solution.

67° F and a relative humidity of 70 per cent for 20 days before being examined. The results of the experiment are tabulated in table 8. Insect mortality was rather closely correlated with the spreading ability of the solution.

In test no. 4, dissolving the toxicant in acetone caused it to be dissolved in the aqueous solution more rapidly and completely when the acetone solution was poured into the water than if the toxicant had been added directly to the water without an intermediary solvent. This was reflected in the improved kill as compared to test no. 3. In test no. 11, the amount of dry blood albumin was about in the proportion in which it is used commercially in the tank-mixture method of using oil spray.

[8] Kagy, J. F. 1931. Report of Crop Protection Institute Investigation, Dow Chemical Company Fellowship. (Unpublished manuscript.) 81 p. On file with the Crop Protection Institute, Durham, N. H.

Figure 9 shows the relation of the insecticidal efficiency of two toxic aqueous solutions to the spreading ability of the solutions as determined by the concentration of the spreader. Curve *A* depicts the increase in mortality of the woolly apple aphid, *Eriosoma lanigerum* (Hausm.), from a 0.025 per cent nicotine solution as the per cent of soft-soap solution was increased from 0.1 to 3.0 (*12*). The increase in mortality of California red scale, *Aonidiella aurantii* (Mask.), from 0.1 per cent solutions of sodium dinitro-o-cyclohexylphenate as the concentration of Vatsol OT was increased from 0.025 to 1.0 per cent is shown in *B*. In either case the limiting factor in the use of the solutions as far as insecticidal efficiency is concerned, is not the toxicity *per se* of the solutions, but the ability of the solutions to penetrate the mat of waxy threads covering the aphids in one case and the waxy capillary system beneath the bodies of the scales in the other.

The sodium dinitro-o-cyclohexylphenate solutions were used in the present experiment only to show the relation of spreading to insecticidal efficiency; the writer does not wish to imply that the toxicant involved shows promise as a practical insecticide for use on citrus trees in the way it was used in the present experiment. As far as is known to date, the phytocidal effect of the compound limits its use in this regard.

SUMMARY

Although the static contact angle may not be a true index of the wetting and spreading properties of a liquid under the dynamic conditions which obtain during the actual spraying operation, it indicates the spreading and penetrating qualities of the liquid after it has been deposited on the plant surface.

An attempt was made to devise a means of contact-angle measurement which would combine practicability and accuracy. Previous methods of contact-angle measurement have been based on the projection or reflection of the image of a solid face immersed in a liquid in such a way that the angle made by the water/air surface with that of the water/solid is at the minimum value of the contact angle, or by the projection of photographic negatives made of drops of liquids resting on solids. Measurements of the contact angle liquid/solid are then made by means of a protractor on the projected or reflected image.

The present method involves the projection of a drop of liquid resting on a perfectly horizontal substratum and the tracing of the projected image. A microprojector built for material mounted on microscope slides was adapted, after minor adjustments, for the purpose of projecting liquid drop outlines.

The outlines of drops 5 mm in diameter were found to be elliptical, but were practically circular for liquids with contact angles less than 65°. Smaller drops retain a spherical shape at even higher contact angles. The contact angles may be derived by differentiation of the equation of the drop outline. If the drop is a segment of a sphere, a more simple method may be employed for calculation of the contact angle.

It was shown statistically that five measurements of the contact angle of a given liquid are sufficient to establish a highly significant mean and that a difference as low as 3° 32′ can be reliably determined. Size of drop had no significant effect on contact angle.

The nature of the substratum was found to have a great influence on the contact angle liquid/solid. Thus, leaves of different plant species, leaves of different ages on the same plant, and different sides or portions of a single leaf cause variation in the contact angle of a given liquid. A great difference in the contact angle of oil on leaf wax and oil on the wax of scale insects was found, the former being the greater.

Various solutes were tested with reference to their effect in lowering the contact angle of water and oil on various solids. The relative spreading ability of solutions on one substratum does not necessarily indicate their relative spreading ability on other substrata. Thus Vatsol OT was found to be a more effective spreader per unit concentration than sodium oleate on *Viburnum* leaves but less effective on beeswax.

According to the formula for rate and distance of penetration of liquids in capillary tubes, a reduction of the surface tension and consequently of the contact angle of a liquid may increase its penetrativity into tubes on the inner surface of which it has a high contact angle, but reduces its penetrativity in tubes on the inner surface of which it has a very low or zero contact angle. This principle was experimentally verified with aqueous solutions in chemically clean glass tubes as contrasted to waxed glass tubes. The practical application of the principle is that by a reduction of surface tension the rate of penetration of aqueous solutions into porous solids such as bark, on which the solutions have a very low contact angle, may be decreased and their rate of penetration through the waxy threads exuded by insects, or under their bodies and into their spiracles, may be increased. Consequently the usual great differences in the rate of penetration of the solutions into insects and their substrata, if they happen to be located on porous bark, is reduced.

The surface tension of water may be sufficiently reduced by the addition of some of the more effective wetting agents so that toxic aqueous solutions can penetrate under the body of the red scale, *Aonidiella aurantii* (Mask.), and cause the death of the insect. The percentage of

mortality of red scale from a given toxicant was found to be correlated with the effectiveness and concentration of the spreading agent; the more effective spreading agents and the higher concentrations resulted in greater insecticidal efficiency of the solution. The penetration of aqueous solutions under the body of the red scale may be demonstrated with the aid of a water-soluble dye.

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